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(21) International Application Number: PCT/GB99/00744 (22) International Filing Date: 22 March 1999 (22.03.99) (30) Priority Data: 9806198.9 24 March 1998 (24.03.98) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CARPENTER, Ian, William [GB/GB]; 52 Park Road, Stapleton, Bristol BS16 1AU (GB). HAYES, John, William [GB/GB]; 5 Elm Court, Sonning Common, Reading RG4 9ND (GB). (74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CATALYTIC GENERATION OF HYDROGEN (57) Abstract A process for the catalytic generation of hydrogen by the self-starting, self-sustaining combination of partial oxidation and steam reforming of dimethyl ether comprises contacting a mixture of the dimethyl ether, an oxygen-containing gas and steam with a precious metal catalyst which is selective for the partial oxidation reaction. Suitable catalysts include platinum or rhodium supported on zirconia or a mixture of ceria and zirconia.		

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CATALYTIC GENERATION OF HYDROGEN

This invention relates to the catalytic generation of hydrogen.

5 Hydrogen is currently used mainly in industry, in activities such as the manufacture of fertilisers, petroleum processing, methanol synthesis, annealing of metals and producing electronic materials. In the foreseeable future, the emergence of fuel cell technology will extend the use of hydrogen to domestic and vehicle applications.

10 A fuel cell works best when the anode is supplied with neat hydrogen. In the design of practical systems, however, other factors also need to be considered, including the availability, cost, supply, distribution, storage and release of clean hydrogen. When all these factors are taken into consideration, alternative methods of fuelling can show an overall advantage.

15 New fuel-processing technologies for generating hydrogen tend to be based either on steam-reforming or on partial oxidation. Each approach has its merits. Partial oxidation is a fast exothermic process, resulting in rapid start-up and short response times. Steam reforming is endothermic and very efficient, producing hydrogen from both the fuel and the
20 steam.

However, our work on system simulations leads us to predict that, in terms of efficiency, the ideal fuel-processor is likely to function by a combination of partial oxidation and steam reforming. In our previous work, (see EP 0217532; EP 0262947; WO 96/00186
25 and Platinum Metals Review, 1989, 33 (3) 118-127), we have shown that the two reactions can be carried out simultaneously in the same catalyst bed using a catalytic hydrogen generator which has become known as the HotSpotTM reactor. The process which takes place in the HotSpot reactor is a self-sustaining combination of exothermic partial oxidation and endothermic steam-reforming to produce a gas-stream containing mainly hydrogen,
30 carbon dioxide and nitrogen, and is characterised by a low rate of carbon monoxide formation.

Possibly, the easiest fuel to process is methanol. However, because of certain disadvantages of methanol, it is by no means certain that methanol will be widely adopted for fuel cell vehicle and domestic applications.

5 An object of the present invention is to provide an improved process for generating hydrogen by oxidatively reforming (*ie* by partial oxidation alone or with the combination of steam reforming) of an organic fuel other than methanol.

10 According to the present invention there is provided a process for the catalytic generation of hydrogen by the self-starting, self-sustaining oxidation of an organic fuel comprising contacting a mixture of dimethyl ether and an oxygen-containing gas and optionally steam with a precious metal catalyst which is selective for the oxidative reforming of organic fuels.

15 Preferably, steam is introduced into the mixture of dimethyl ether and oxygen-containing gas after the self-starting, self-sustaining partial oxidation of the dimethyl ether has commenced.

20 Further preferably, the oxygen-containing gas is air.

A suitable catalyst for the process of the invention is platinum or rhodium supported on zirconia or a mixture of ceria and zirconia.

25 Preferably, platinum or rhodium comprises 0.1 weight% to 5 weight% of the total weight of the supported catalyst.

Further preferably, the weight ratio of ceria to zirconia in the catalyst support material is from 0.5 to 99.5 to 99.5 to 0.5.

30 The present invention is also hydrogen whenever prepared according to the process defined above.

An advantageous feature of the process of the present invention is that it provides for a highly compact and responsive fuel processing unit characterised by the absence of separate or integral shift reactors.

5 As an alternative to methanol, dimethyl ether (DME) has several further advantages, namely:

- (i) it has much lower toxicity;
- (ii) it is less hygroscopic, making it less corrosive;
- (iii) it has a higher energy density; and
- 10 (iv) although a gas at ambient temperatures, it is easy to liquify.

Furthermore, as dimethyl ether has a high cetane number and combusts cleanly, it is being assessed as an alternative to conventional diesel fuel. Should this happen, it can be expected to become much more widely available than methanol.

15

Dimethyl ether can be used either as a fuel in its own right or as a promoter for liquified hydrocarbon fuels (eg LPG) that are more difficult to convert to hydrogen. The dimethyl ether promotes start-up from ambient temperature.

20 The present invention is further described by way of the following illustrative Examples.

EXAMPLE 1

25 A batch of catalyst with a nominal composition of 1%Pt/ZrO₂ (based on the proportions of precursors) was made by impregnating 20g of zirconia. The impregnating solution was prepared by dissolving 0.4g tetraammineplatinum(II) hydrogencarbonate in 16cm³ of citric acid (100g l⁻¹).

30 The impregnating solution was added to the support material, and mixed thoroughly. The resultant paste was dried at 120°C for 8 hours, before being calcined in static air at

500°C for 2 hours. Finally, the catalyst was crushed and sieved. No special activation was required prior to testing.

5 A small bed (0.2g) of the catalyst was loaded into a tubular quartz reactor, which was positioned at the centre of a tubular furnace. A mixture of gas-phase DME (5 standard cm³ min⁻¹) and air (11 cm³ min⁻¹) was passed through the catalyst bed, while the temperature inside the furnace was raised at 2°C min⁻¹. As partial oxidation started to occur as soon as the gas stream came into contact with the catalyst, the H₂O feed stream (steam : 31 cm³ min⁻¹, nitrogen : 112 cm³ min⁻¹) was turned on almost immediately (within 10 seconds of starting).

15 The rate of hydrogen production was highest when the catalyst bed temperature reached 370°C. At this temperature, the product gas-stream contained 18% H₂, 6.6% CO₂, 1.3% CO, 4% CH₄ and 65% N₂ (plus water). The reaction was self-sustaining, with hydrogen production continuing even when the furnace was switched off.

EXAMPLE 2

20 A batch of catalyst with a nominal composition of 1%Rh/CeO₂-ZrO₂ (based on the proportions of precursors) was prepared by impregnating 50g of 50:50 (by mass) ceria-zirconia support material with an aqueous Rh-salt solution. The impregnating solution (30 cm³) was prepared by adding distilled water to 3.64g of aqueous rhodium(III) nitrate (from Johnson Matthey) containing 0.5g rhodium.

25 The impregnating solution was added to the support material, and mixed thoroughly. Excess water was removed from the edge of the resultant paste, which was then left for 2 hours to form a semi-rigid cake. After breaking-up the cake, the lumps were dried at 120°C for 8 hours, before being calcined in static air at 500°C for 2 hours. Finally, the catalyst was crushed and sieved. No special activation was required prior to testing.

A small bed (0.2g) of the catalyst was loaded into a tubular quartz reactor, which was positioned at the centre of a tubular furnace. A mixture of gas-phase DME ($6.5 \text{ standard cm}^3 \text{ min}^{-1}$) and air ($11 \text{ cm}^3 \text{ min}^{-1}$) was passed through the catalyst bed, while the temperature inside the furnace was raised at 2°C min^{-1} . As in Example 1, partial oxidation started to occur as soon as the gas stream came into contact with the catalyst, and so the H_2O feed (steam : $31 \text{ cm}^3 \text{ min}^{-1}$, nitrogen : $112 \text{ cm}^3 \text{ min}^{-1}$) was turned on almost immediately (within 10 seconds of starting).

The rate of hydrogen production was highest when the catalyst bed temperature reached 540°C . At this temperature, the product gas-stream contained 21% H_2 , 4.7% CO_2 , 2.1% CO , 1% CH_4 and 69% N_2 (plus water). The reaction was self-sustaining, with hydrogen production continuing even when the furnace was switched off.

CLAIMS

1. A process for the catalytic generation of hydrogen by the self-starting, self-sustaining oxidation of an organic fuel comprising contacting a mixture of dimethyl ether and an oxygen-containing gas and optionally steam with a precious metal catalyst which is selective for the oxidative reforming of organic fuels.
5
2. A process according to claim 1 wherein steam is introduced into the mixture of dimethyl ether and oxygen-containing gas after the self-starting, self-sustaining partial oxidation of the dimethyl ether has commenced.
10
3. A process according to claim 1 or 2 wherein the oxygen-containing gas is air.
4. A process according to any one of the preceding claims wherein the catalyst is platinum or rhodium supported on zirconia or a mixture of ceria and zirconia.
15
5. A process according to claim 4 wherein platinum or rhodium comprises 0.1 weight% to 5 weight% of the total weight of the supported catalyst.
- 20 6. A process according to claim 4 or 5 wherein the weight ratio of ceria to zirconia in the catalyst support material is from 0.5 to 99.5 to 99.5 to 0.5.
7. Hydrogen whenever prepared by a process according to any one of the preceding claims.
25
8. A fuel cell system comprising a hydrogen production unit which operates according to the process of any one of claims 1 to 6.

INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/GB 99/00744

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 626 794 A (BHATTACHARYYA ALAKANANDA ET AL) 6 May 1997 see claim 1	1
A,P	US 5 741 474 A (ISOMURA MANABU ET AL) 21 April 1998 see column 3; line 11 - column 5, line 25	1
A	WO 96 00186 A (JOHNSON MATTHEY PLC ; EDWARDS NEIL (GB); FROST JONATHON CHARLES (GB) 4 January 1996 see page 4, line 1 - page 5, line 14	1
A	US 4 859 434 A (ROBERTS GEORGE W ET AL) 22 August 1989 see claim 1	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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